PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

NOVEMBER 1999 SAMPLING EVENT

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Pesticide Monitoring Project Report
November 1999 Sampling Event

Executive Summary

As part of the District's quarterly ambient monitoring program, unfiltered water and sediment samples from 37 sites were collected from November 8 to November 18, 1999 and analyzed for over sixty pesticides and/or products of their degradation. The herbicides ametryn, atrazine, bromacil, hexazinone, metolachlor, metribuzin, norflurazon, and simazine, along with the insecticides/degradates atrazine desethyl, atrazine desisopropyl, diazinon, beta endosulfan, and endosulfan sulfate were detected in one or more of these surface water samples. The diazinon concentration detected (0.059 µg/L at S38B), should not have an acute, detrimental impact for fish. However, for aquatic invertebrates, this level is slightly greater than the calculated chronic toxicity (0.04 µg/L) for *Daphnia magna*, a sensitive indicator species for aquatic macroinvertebrates. At this concentration, long term exposure can cause impacts to the macroinvertebrate populations, but the pulsed nature of urban and agricultural runoff releases to the canal system precludes drawing any conclusions about long term average exposures.

The herbicides ametryn and bromacil, along with the insecticides/degradates DDD, DDE, DDT, ethion, and heptachlor, were found in the sediment at several locations, along with two PCB compounds. Some of the detected sediment concentrations of DDD and DDE are usually associated with the potential for impacting wildlife when compared to coastal sediment quality assessment guidelines. The DDT and two of the DDD detections were of a magnitude considered to represent significant and immediate hazard to aquatic organisms. There are no corresponding freshwater sediment quality assessment guidelines, however. The compounds and concentrations found are typical of those expected from intensive agricultural activity.

Background and Methods

The District's pesticide monitoring network includes stations designated in the Everglades National Park Memorandum of Agreement, the Miccosukee Tribe Memorandum of Agreement, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Project (non-ECP) permit. Surface waters are sampled quarterly and sediments semiannually.

Sixty-six pesticides and degradation products were analyzed for in samples from all of the 37 sites (Figure 1). Site GORDYRD was added to evaluate water quality in the Ten Mile Creek basin. Ten Mile Creek is the major tributary of the North Fork of the St. Lucie River, an Outstanding Florida Water (OFW). The analytes, their respective minimum detection limits (MDL), and practical quantitation limits (PQL) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee Florida. The reader is referred to the *Quality Assurance Evaluation* section of this report for a summary of any limitations on data validity that might influence the uses to which these data may be put. Each pesticide's description and possible uses and sites of application are taken from Hartley and Kidd (1987). The Florida Ground Water Guidance Concentrations (FDEP, 1994a) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, dermal uptake). Primary ground water standards are enforceable ground water standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the USEPA under Section 304 (a) of the Clean Water Act, if available, or the lowest EC_{50} or LC_{50} reported in the summarized literature. Sediment concentrations are compared to coastal sediment quality assessment guidelines (FDEP, 1994b), as there are no corresponding freshwater sediment quality assessment guidelines. A value below the threshold effects level (TEL) should not have an impact on wildlife. The value between the TEL and probable effects level (PEL) has a possibility for impacts, while those exceeding the PEL have a substantial probability for impacting wildlife. This summary covers surface water and sediment samples collected between November 8 and November 18, 1999.

Findings and Recommendations

At least one pesticide was detected in surface water and sediment at 31 and 18, of the 37 and 34 sites, respectively. Sediment samples are not collected at GORDYRD, C51SR7 and CR33.5T. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All these compounds have previously been detected in this monitoring program.

The diazinon concentration detected (0.059 μg/L at S38B), should not have an acute, detrimental impact for fish. However, for aquatic invertebrates, this level is slightly greater than the calculated chronic toxicity (0.04 μg/L) for *Daphnia magna*, a sensitive indicator species for aquatic macroinvertebrates. At this concentration, long term exposure can cause impacts to the macroinvertebrate populations, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about long term average exposures.

No ethion was detected in the surface water at S99 (Figure 2). Since October 1995, eight out of seventeen sampling events had a detectable level of ethion. With the method detection limit around 0.02 μg/L, any detection will automatically exceed the calculated chronic toxicity (0.003 μg/L). Ethion was detected in the sediment at S99 (4.6 μg/Kg) and S176 (7.1. μg/Kg). However, no sediment quality assessment guidelines have been developed for ethion.

The only endosulfan (α plus β) surface water concentration detected (GORDYRD) during this sampling event does not exceed the Florida Class III surface water quality standard (Chapter 62-302) of 0.056 μg/L. This is the first time sampling at this location. No endosulfan was detected at S178. Since January 1996, 15 sampling events at S178 have been performed without an exceedance of the water quality standard (Figure 3). No endosulfan was quantified in the sediment.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly with relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 μg/L (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC_{50} of 14.1 mg/L for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.0097 to 0.058 μg/L. Using these criteria, these surface water levels should not have an acute, detrimental impact on fish or aquatic invertebrates. The sediment concentrations ranged from 3.5 to 23.5 μg/Kg. However, no sediment quality assessment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μg/L for bluegill and fathead minnow (Verschueren, 1983). Atrazine inhibits cell multiplication of the alga, *Microcystis aeruginosa*, at 3 μg/L and most other biological effects occur at higher concentrations (Verschueren, 1983). The atrazine surface water concentrations found in this sampling event ranged from 0.010 to 0.53 μg/L. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates. Atrazine was not quantified in the sediment.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio, on a molar basis, (DAR) has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.2) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). The one exception to this is the S178 location, where the DAR value is 0.6, suggesting the atrazine has been degraded significantly into it's primary metabolite. This would be consistent with the standing water conditions that frequently occur in the canal upstream of S178. No appreciable difference can be detected when the DAR is determined on the basis of flow or no flow (Table 6). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the south Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC_{50} of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was 0.19 µg/L. Using these criteria, these levels should not have an acute or chronic detrimental impact on fish. Bromacil was quantified in the sediment at three sites. The sediment concentration ranged from 43 to 130 µg/Kg. However, no sediment quality assessment guidelines have been developed for bromacil.

DDE, DDD, DDT: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2,2-bis(4-chlorophenyl)-1,1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyl**t**richloroethane), a popular insecticide for which the USEPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds accounts for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioaccumulation factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

Sediment quality assessment guidelines have been developed for several metals and organic compounds in coastal sediments (FDEP, 1994b). The TEL is 2.1 µg/Kg and the PEL is 374 µg/Kg for DDE in coastal sediments. All but one of the DDE concentrations detected (1.7 to 67 µg/Kg) are between the TEL and PEL. The 1.7 µg/Kg value (S331), which is below the TEL, should not have an impact on wildlife. The levels between the TEL and PEL have the possibility for impacting wildlife as they have exceeded the threshold level.

The DDD concentrations detected range from 2.2 to 15 µg/Kg. Those values, which are between the TEL (1.2 µg/Kg) and PEL (7.8 µg/Kg), have the possibility for impacting wildlife. Two of the values (9.4 µg/Kg at S2 and 15 µg/Kg at S6) exceed the PEL and are considered to represent significant and immediate hazard to aquatic organisms.

The only DDT concentration detected (10 µg/Kg at S6) exceeds the PEL (4.8 µg/Kg). This level is considered to represent a significant and immediate hazard to aquatic organisms.

Diazinon: Diazinon is a non-systemic insecticide and acaricide registered for use on a wide range of crops including citrus, bananas, vegetables, potatoes, sugarcane, rice and ornamentals. Environmental fate and toxicity data in Tables 4 and 5 indicate that diazinon (1) is easily lost from soil by surface solution, with a moderate loss from leaching, and minimum loss from surface adsorption; (2) is slightly toxic to mammals and relatively toxic to fish; and (3) does not bioaccumulate significantly. The diazinon concentration detected (0.059 µg/L at S38B) should not have an acute, detrimental impact on fish. However, for aquatic invertebrates, this level is slightly greater than the calculated chronic toxicity (0.04 μg/L) for *Daphnia magna*, a sensitive indicator species for aquatic macroinvertebrates. At this concentration, long term exposure can cause impacts to the macroinvertebrate populations.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, the α (alpha) and the β (beta) forms. Endosulfan is highly toxic to mammals, with an acute oral LD_{50} for rats of 70 mg/kg (Hartley and Kidd, 1987). The Soil Conservation Service rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 4). β-endosulfan's water solubility and Henry's constant indicate volatilization may be significant in shallow waters. A bioconcentration factor of 1,267 indicates a low to moderate degree of accumulation in aquatic organisms (Lyman et al., 1990). The only endosulfan (α plus β) surface water concentration detected (GORDYRD) during this sampling event does not exceed the Florida Class III surface water quality standard (Chapter 62-302) of 0.056 μg/L. This is the first time sampling at this location. No endosulfan was detected at S178. Since January 1996, 15 sampling events have been performed without an exceedance of the water quality standard (Figure 3). No endosulfan was quantified in the sediment.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's constant indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Lyman et al., 1990). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). The surface water concentration detected in this sampling event was 0.024 μg/L (GORDYRD). No FDEP surface water standard (FAC 62-302) has been promulgated for endosulfan sulfate, nor does this concentration exceed the Florida Class III surface water quality standard of 0.056 μg/L, for the parent compound, endosulfan. No surface water residue of endosulfan sulfate was detected at S178 (Figure 3). No endosulfan sulfate was quantified in the sediment.

Ethion: Ethion is a non-systemic acaricide and insecticide registered for use on several fruits, citrus, and vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that ethion (1) is strongly sorbed to soil and therefore can accumulate in sediments; (2) is slightly toxic to mammals, relatively toxic to fish and extremely toxic to Daphnia; and (3) bioconcentrates to a limited extent. Several sources of toxicity information have shown both agreement and disagreement of these laboratory tests. Ethion was detected in the sediment at S99 (4.6 μg/Kg) and S176 (7.1 μg/Kg). However, no sediment quality assessment guidelines have been developed for ethion. No ethion was detected in the surface water at any of the sampling sites. Since October 1995, eight out of seventeen sampling events at S99 had a detectable level of ethion in the surface water (Figure 2). With the method detection limit around 0.02 μg/L, any detection will automatically exceed the calculated chronic toxicity (0.003 μg/L) for *Daphnia magna*.

Heptachlor: Heptachlor is a restricted use chlorinated hydrocarbon insecticide. Sales in the United States were suspended in August of 1987 and all registrations were cancelled due to its potential carcinogenicity, with the exception of the control of fire ants in certain underground utility closures. Heptachlor was registered for use in the control of termites, ants, and soil insects. Heptachlor is extremely toxic to aquatic organisms and birds (U. S. Environmental Protection Agency, 1986). Heptachlor is considered persistent and bioaccumulates (Table 4). Heptachlor is not expected to leach, since it is insoluble in water and should absorb to the soil surface; thus it should not reach underground aquifers (U. S. Environmental Protection Agency, 1986). Heptachlor was detected in the sediment at only one site (US41-25 at 1.9 μg/Kg). However, insufficient data were available to develop sediment quality assessment guidelines for heptachlor (FDEP, 1994b).

<u>Hexazinone</u>: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/l for *Daphnia magna* (U.S. Environmental Protection Agency, 1988). The surface water concentrations found in this sampling event ranged from 0.019 to 0.037 μg/L and should not have an acute impact on fish or aquatic invertebrates. Hexazinone was not detected in the sediment.

<u>Metolachlor</u>: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only concentration of metolachlor detected was 0.059 μg/L at S5A (Table 2). This is more than three orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have a harmful impact on fish or aquatic invertebrates.

<u>Metribuzin</u>: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in Tables 4 and 5 indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metribuzin detected was 0.026 μg/L (S190). Using these criteria, this surface water level should not have an acute impact on fish or aquatic invertebrates. No metribuzin was detected in the sediment.

<u>Norflurazon</u>: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC_{50} for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.030 to 0.84 μg/L. Even at the highest concentration, this is over two orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute,

detrimental impact on fish or aquatic invertebrates.

PCBs: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1254 and PCB-1260 are a commercial grade mixture containing 54% and 60%, respectively, chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the adsorbent. While the production ban, phase out of uses, and stringent spill clean-up requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and bioaccumulate in fish, make this class of organochlorine compounds especially problematic. Florida sediment quality assessment guidelines has been developed for total PCBs in coastal sediments (FDEP, 1994b). However, an evaluation of the reliability of the sediment quality assessment guidelines for total PCBs suggests a low degree of confidence can be placed on these guidelines due to the insufficient data used in their development. The TEL is 21.6 µg/Kg and the PEL 189 µg/Kg for PCB's. The sediment residue detected at S7 of 94.5 µg/Kg, has a possibility for impacting wildlife, while the concentration at S80 of 620 µg/Kg has a strong probability for impacting wildlife. None of the PCB congeners were detected in the surface water.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. Environmental Protection Agency, 1984). The highest surface water concentration of simazine found in this sampling event was 0.034 µg/L, far below any level of concern for fish or aquatic invertebrates.

Quality Assurance Evaluation

Four duplicate samples were collected at sites S31, S7, S3, and S332. All the analytes detected in the surface water had precision ≤30% RPD. No analytes were detected in the field blanks collected at S332 and S3. No analytes were detected in the three equipment blanks performed at S38B, S140, and G94D. All samples were shipped and all bottles were received.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted. The organochlorine parameters failed precision measurements (relative percent difference) for the surface water samples at the following locations: S38B, S142, G123, S9, S31 (including field duplicate), S12C, US4125, G211, S331, S176, S332, S177, S178, and S18C. The percent recovery of the lab fortified blank for methamidophos and monocrotophos failed appropriate criteria at the same locations. Methamidophos also failed fortified blank recoveries for the sediment samples collected at: S80, S99, S65E, S191, FECSR78, S78, S79, S235, S4, S3, (including field duplicate), and S2. The sediment sample collected at ACME1DS was held beyond holding time due to the need for reextraction for the organochlorine and organonitrogen/phosphorus pesticides. Comparisons are based on the FDEP Comprehensive Quality Assurance Plan targets for precision and accuracy. Organic quality assurance targets are set according to historically generated data or are adapted from the U.S. Environmental Protection Agency with slight modifications or internal goals, based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these analyses and interpretation of the respective analytical results should consider this effect. It has recently been brought to the attention of the Pesticide Program Manager that the sample collection procedure for pesticides employed a triple rinsing of the sample bottles, a procedure which has the potential for biasing the ambient concentration higher, relative to what would be representative of the surface water sample. The bias is based on the contention that the analytical laboratory performs a whole sample extraction and a solvent rinse of the bottle inner surface. This situation is currently being investigated.

Glossary

LD_{50}: The dosage which is lethal to 50% of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LC_{50}: A concentration which is lethal to 50% of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

EC_{50}: A concentration necessary for 50% of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Koc: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:
The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:
The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

MDL: The minimum concentration of an analyte that can be detected with 99% confidence of its presence in the sample matrix.

PQL: The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQL is further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15%. In general, the PQL is 2 to 5 times larger than the MDL.

TEL: The threshold effects level represents the upper limit of the range of sediment contaminant concentrations dominated by no effect data entries, or the minimal effects range. Within this range, concentrations of sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms

PEL: The probable effects level was calculated to define the lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects or the lower limit of the probable effects range. Within the probable effects range, concentrations of sediment-associated contaminants are considered to represent significant and immediate hazards to aquatic organisms.

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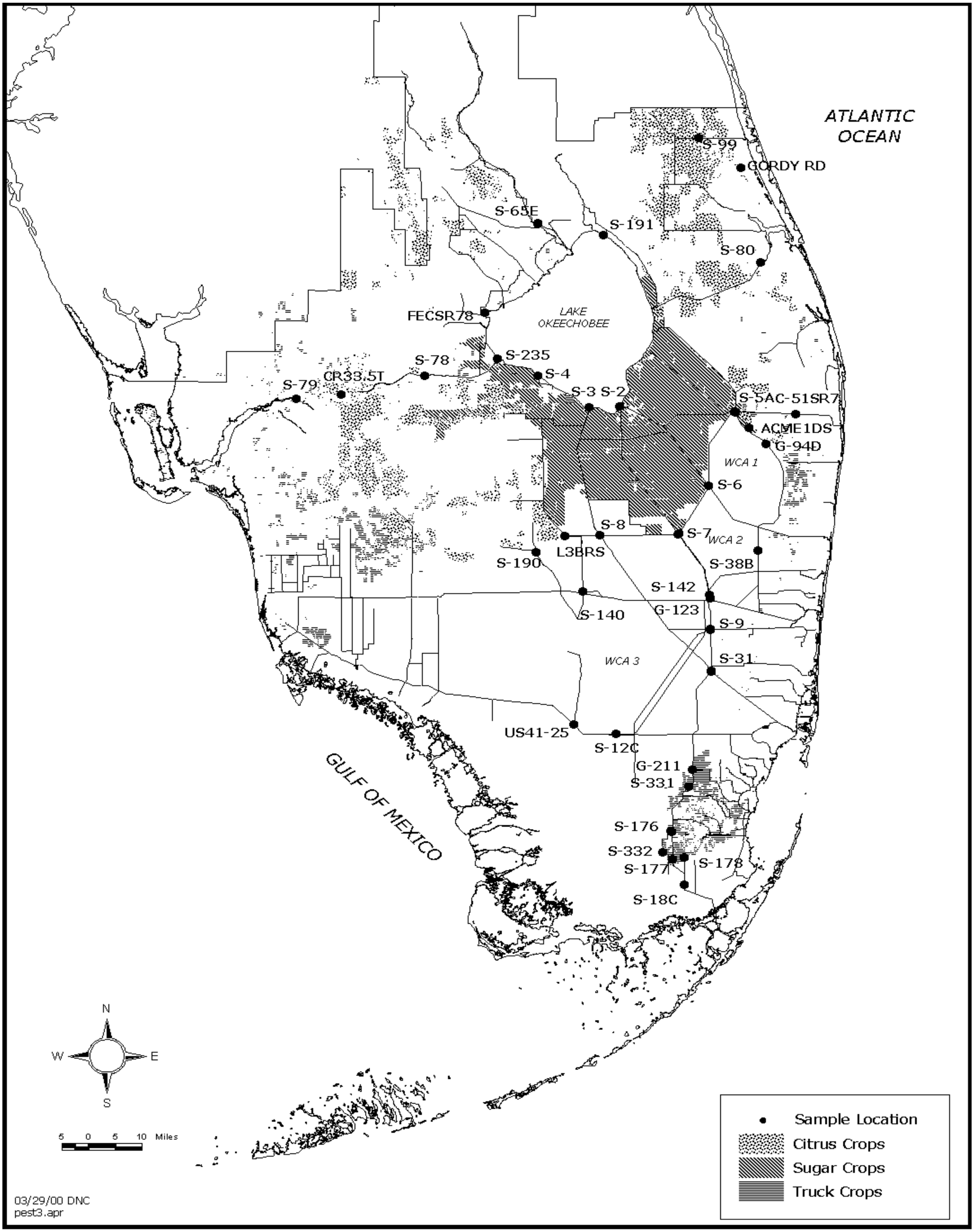

Figure 1. SFWMD Pesticide Monitoring Network

Table 1. Minimum detection limits (MDL) and practical quantitation limits (PQL) for pesticides determined in November 1999.

Pesticide or degradation product	Water range of MDL-PQL (µg/L)	Sediment range of MDL-PQL (µg/Kg)	Pesticide or degradation product	Water range of MDL-PQL (µg/L)	Sediment range of MDL-PQL (µg/Kg)
2,4-D	2 - 4	33 – 420	endosulfan sulfate	0.0019 - 0.01	0.85 - 9.7
2,4,5-T	2 - 4	33 – 420	endrin	0.0019 - 0.01	1.7 - 38
2,4,5-TP (silvex)	2 - 4	33 – 420	endrin aldehyde	0.0019 - 0.01	0.85 - 19
alachlor	0.048 - 0.25	12 – 290	ethion	0.019 - 0.1	1.9 - 48
aldrin	0.00094 - 0.005	0.49 - 9.8	ethoprop	0.019 - 0.1	4.0 - 98
ametryn	0.0094 - 0.05	1.9 - 48	fenamiphos (nemacur)	0.029 - 0.15	12 - 290
atrazine	0.0094 - 0.05	1.9 - 48	fonofos (dyfonate)	0.019 - 0.1	4.0 - 48
atrazine desethyl	0.0094 - 0.05	NA	heptachlor	0.00095 - 0.005	0.49 - 9.8
atrazine desisopropyl	0.0094 - 0.05	NA	heptachlor epoxide	0.00095 - 0.01	0.49 - 9.8
azinphos methyl (guthion)	0.019 - 0.010	2.0 – 190	hexazinone	0.019 - 0.1	8.1- 190
α-BHC (alpha)	0.00094 - 0.005	0.49 - 9.8	imidacloprid	0.4 - 0.8	NA
β-BHC (beta)	0.0019 - 0.010	0.49 - 9.8	linuron	0.4 – 0.8	8.1 - 77
δ-BHC (delta)	0.00094 - 0.005	0.85 - 9.7	malathion	0.029 - 0.15	6.1 - 98
γ-BHC (gamma) (lindane)	0.00094 - 0.005	0.49 - 9.8	metalaxyl	0.057 - 0.3	1.3 - 66
bromacil	0.038 - 0.20	12 – 290	methamidophos	NA	41 – 380
butylate	0.019 - 0.10	NA	methoxychlor	0.0038 - 0.04	2.1 - 77
carbophenothion (trithion)	0.029 - 0.03	1.2 – 38	metolachlor	0.048 - 0.25	21 – 290
chlordane	0.0094 - 0.10	6.1 – 190	metribuzin	0.019 – 0.1	8.1 – 190
chlorothalonil	0.019 - 0.02	0.85 - 38	mevinphos	0.038 - 0.2	9.8 – 250
chlorpyrifos ethyl	0.019 - 0.10	4.1 – 98	mirex	0.0019 – 0.01	0.85 - 19
chlorpyrifos methyl	0.019 - 0.10	4.1 – 98	monocrotophos (azodrin)	NA	81 – 770
cypermethrin	0.0048 - 0.05	ND	naled	0.076 - 0.4	33 – 290
DDD-p,p’	0.0019 - 0.01	0.85 - 19	norflurazon	0.029 - 0.15	12 – 290
DDE-p,p’	0.0019 - 0.01	0.85 - 19	parathion ethyl	0.019 - 0.1	4.0 – 98
DDT-p,p’	0.0019 - 0.01	1.2 – 19	parathion methyl	0.019 - 0.1	4.0 – 98
demeton	0.094 - 0.50	40 – 960	PCB	0.019 - 0.1	9.5 – 290
diazinon	0.019 - 0.10	4.0 – 48	permethrin	0.048 - 0.02	NA
dicofol (kelthane)	0.019 - 0.04	0.85 - 75	phorate	0.029 - 0.15	4.0 – 48
dieldrin	0.0019 - 0.005	0.49 - 9.8	prometryn	0.019 - 0.1	4.0 – 98
disulfoton	0.029 - 0.15	6.1 – 98	simazine	0.019 - 0.1	2.1 – 48
diuron	0.4 - 0.8	8.1 – 77	toxaphene	0.071 - 0.3	30 – 430
α-endosulfan (alpha)	0.0019 - 0.01	0.49 - 9.8	trifluralin	0.0095 - 0.01	1.6 - 38
β-endosulfan (beta)	0.0019 - 0.01	0.49 - 9.8	zinc phosphide	0.50 - 2.0	NA

NA – not analyzed

Table 2. Summary of pesticide residues above the method detection limit found in surface water samples collected by SFWMD in November 1999.

DATE	SITE	FLOW	COMPOUNDS (µg/L)													Number of compounds detected at site
			ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	diazinon	beta endosulfan	endosulfan sulfate	hexazinone	metolachlor	metribuzin	norflurazon	simazine	
11/08/99	S38B	N	-	0.53	0.038 I	-	-	0.059 I	-	-	-	-	-	-	-	3
	S142	N	0.014 I	0.011 I	-	-	-	-	-	-	-	-	-	-	-	2
	G123	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S9	Y	-	0.11	-	-	-	-	-	-	0.019 I	-	-	-	-	2
	S31	N	-	0.021 *	-	-	-	-	-	-	-	-	-	-	-	1
	S12C	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	US41-25	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	G211	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	0
11/09/99	S331	Y	-	0.010 I	-	-	-	-	-	-	-	-	-	-	-	1
	S176	N	-	0.044 I	0.0099 I	-	-	-	-	-	-	-	-	-	-	2
	S332	Y	-	0.033 * I	-	-	-	-	-	-	-	-	-	-	-	1
	S177	N	-	0.019 I	-	-	-	-	-	-	-	-	-	-	-	1
	S178	N	-	0.019 I	0.010 I	-	-	-	-	-	-	-	-	-	-	2
	S18C	Y	-	0.018 I	-	-	-	-	-	-	-	-	-	-	-	1
11/15/99	S140	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S190	Y	-	-	-	-	-	-	-	-	-	-	0.026 I	0.038 I	-	2
	L3BRS	Y	-	0.046 I	-	-	-	-	-	-	-	-	-	0.043 I	-	2
	S8	N	-	0.026 I	-	-	-	-	-	-	-	-	-	-	-	1
	S7	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S6	N	0.058	0.082	-	-	-	-	-	-	0.026 I	-	-	-	-	3
	S5A	N	0.056	0.26	-	-	-	-	-	-	-	0.059 I	-	-	0.028 I	4
11/16/99	GORDYRD	Y	-	-	-	0.014 I	0.14 I	-	0.0034 I	0.024	-	-	-	0.80	0.034 I	6
	S99	Y	-	-	-	-	0.19 I	-	-	-	-	-	-	0.84	0.025 I	3
	S65E	N	-	0.04 I	-	-	-	-	-	-	-	-	-	-	-	1
	S191	N	-	-	-	-	0.15 I	-	-	-	-	-	-	-	-	1
	FECSR78	Y	-	-	-	-	-	-	-	-	0.034 I	-	-	-	-	1
	S78	Y	-	0.061	0.01 I	-	-	-	-	-	-	-	-	-	-	2
	CR33.5T	Y	-	0.070	0.013 I	-	0.11 I	-	-	-	-	-	-	0.030 I	-	4
	S79	Y	-	0.065	0.013 I	-	0.070 I	-	-	-	-	-	-	0.035 I	-	4
11/17/99	S235	R	0.010 I	0.072	0.015 I	-	-	-	-	-	-	-	-	-	-	3
	S4	N	0.014	0.12	-	-	-	-	-	-	0.023 I	-	-	-	-	3
	S3	N	0.029 * I	0.12 *	0.014 * I	-	-	-	-	-	-	-	-	-	-	3
	S2	N	0.022 I	0.11	0.022 I	-	-	-	-	-	-	-	-	-	-	3
	S80	Y	0.0097 I	0.13	0.027 I	-	-	-	-	-	-	-	-	0.051 I	-	4
11/18/99	G94D	Y	0.039 I	0.037 I	-	-	-	-	-	-	-	-	-	-	-	2
	ACME1DS	Y	0.055	0.040 I	-	-	-	-	-	-	0.037 I	-	-	-	-	3
	C51SR7	Y	0.048	0.21	-	-	-	-	-	-	-	-	-	-	-	2
Total number of compound detections			11	26	10	1	5	1	1	1	5	1	1	7	3	

N – no Y – yes R – reverse - denotes that the result is below the MDL; * - results are the average of duplicate samples; I - value reported is less than the minimum quantitation limit, and greater than or equal to the minimum detection limit

Table 3. Summary of pesticide residues above the method detection limit found in sediment samples collected by SFWMD in November 1999.

DATE	SITE	FLOW	COMPOUNDS (μg/Kg)									Number of compounds detected at site
			ametryn	bromacil	DDD	DDE	DDT	ethion	heptachlor	PCB1254	PCB1260	
11/08/99	S38B	N	-	43 I	-	-	-	-	-	-	-	1
	S142	N	-	-	-	9.3	-	-	-	-	-	1
	S31	N	-	-	-	5.3 * I	-	-	-	-	-	1
	US41-25	Y	-	-	-	-	-	-	1.9 I	-	-	1
11/09/99	S331	Y	-	-	-	1.7 I	-	-	-	-	-	1
	S176	N	-	57 I	-	2.1 I	-	7.1 I	-	-	-	3
	S177	N	-	-	2.7 I	22	-	-	-	-	-	2
	S178	N	-	130 I	-	67	-	-	-	-	-	2
11/15/99	S8	N	4.6 I	-	-	4.5 I	-	-	-	-	-	2
	S7	N	23.5 * I	-	3.0 * I	8.65 *	-	-	-	-	94.5 *	4
	S6	N	9.8 I	-	15	43	10 I	-	-	-	-	4
	S5A	N	3.5 I	-	5.8 I	16	-	-	-	-	-	3
11/16/99	S99	Y	-	-	-	8.4	-	4.6 I	-	-	-	2
	S79	Y	-	-	-	14 I	-	-	-	-	-	1
11/17/99	S4	N	17 I	-	-	11	-	-	-	-	-	2
	S3	N	-	-	2.2 * I	7.45*	-	-	-	-	-	2
	S2	N	12 I	-	9.4 I	37	-	-	-	-	-	3
	S80	Y	-	-	-	-	-	-	-	620	-	1
Total number of compound detections			6	3	6	15	1	2	1	1	1	

N – no Y – yes R – reverse - denotes that the result is below the MDL; * - results are the average of duplicate samples; I - value reported is less than the minimum quantitation limit, and greater than or equal to the minimum detection limit

Table 4. Selected properties of pesticides found in the November 1999 sampling event.

Common name	FDEP Surface Water Standards 62-302 (µg/L)	Florida Ground Water Guidance Conc. (µg/L)	LD_{50} acute rats oral (mg/Kg) (1)	EPA carcinogenic potential	Water Solubility (mg/L) (2, 3)	Koc (ml/g) (2, 3)	soil half-life (days) (2, 3)	SCS rating (2) LE	SA	SS	Bioconcentration Factor (BCF)
ametryn	-	63	1,110	D	185	300	60	M	M	M	33
atrazine	-	3**	3,080	C	33	100	60	L	M	L	86
bromacil	-	90	5,200	C	700	32	60	L	M	M	15
diazinon	-	6.3	240 - 480	E	40	570	40	M	S	L	77
DDD-P,P'	-	0.1	3,400	-	0.055	239,900	-	-	-	-	3,173
DDE-P,P'	-	0.1	880	-	0.065	243,220	-	-	-	-	2,887
DDT-P,P'	0.001	0.1	113	-	0.00335	140,000	-	-	-	-	15,377
endosulfan, beta	0.056	0.35	70	-	0.28	-	-	-	-	-	1,267
endosulfan sulfate	-	0.3	-	-	0.117	-	-	-	-	-	2,073
ethion	-	3.5	208	-	1.1	8,900	150	S	L	M	586
heptachlor	0.00021	0.4**	147 - 220	B2	0.18	-	-	-	-	-	1,626
hexazinone	-	231	1,690	D	33,000	54	90	L	M	M	2
metolachlor	-	70	2,780	C	530	200	90	L	M	M	18
metribuzin	-	175	2,200	D	1,220	41	30	L	S	M	11
norflurazon	-	280	9,400	-	28	700	90	M	M	L	94
PCB	0.014	0.5**	-	B2	-	-	-	-	-	-	-
simazine	-	4**	>5,000	C	6.2	130	60	L	M	M	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large (L), medium (M), small (S) or extra small (XS)
Bioconcentration Factor (BCF) calculated as BCF = 10^(2.791 - 0.564 log WS) (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP surface water standards (12/96) for Class III water except Class I in ( )
**primary standard

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Table 5. Toxicity of pesticides found in the November 1999 sampling event to selected freshwater aquatic invertebrates and fishes (ug/L).

Common name	48 hr EC_{50} Water flea *Daphnia Magna*		acute toxicity (*)	chronic toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales Promelas*		acute toxicity	chronic toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*		acute toxicity	chronic toxicity	96 hr LC_{50} Largemouth Bass *Micropterus salmoides*		acute toxicity	chronic toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*		acute toxicity	chronic toxicity	96 hr LC_{50} Channel Catfish *Ictalurus punctatus*		acute toxicity	chronic toxicity
ametryn	28,000	(6)	9,333	1,400	-		-	-	4,100	(4)	1,367	205	-		-	-	8,800	(4)	2,933	440	-		-	-
atrazine	6,900	(6)	2,300	345	15,000	(6)	5,000	750	16,000	(4)	5,333	800	-		-	-	8,800	(4)	2,933	440	7,600	(4)	2,533	380
bromacil	-		-	-	-		-	-	127,000	(6)	42,333	6,350	-		-	-	36,000	(6)	12,000	1,800	-		-	-
diazinon	0.8	(1)	0.3	0.04	7,800	(6)	2,600	390	168	(1)	56	8.4	-		-	-	90	(1)	30	4.5	-		-	-
	0.9	(8)	0.3	0.045	-		-	-	165	(3)	56	8.3	-		-	-	1,650	(3)	550	83	-		-	-
	-		-	-	-		-	-	16,000	(4)	5,333	800	-		-	-	2,900	(4)	967	145	-		-	-
DDD-P,P'	3,200	(7)	1,067	0.04	4,400	(1)	1,467	220	42	(1)	14	2.1	42	(1)	14	2.1	70	(1)	23.3	3.5	1,500	(1)	500	75
DDE-P,P'	-		-	-	-		-	-	240	(1)	80	12	-		-	-	32	(1)	10.7	1.6	-		-	-
DDT-P,P'	-		-	-	19	(5)	6.3	0.95	8	(5)	2.7	0.4	2	(5)	0.7	0.10	7	(5)	2.3	0.35	16	(5)	5.3	0.8
endosulfan	166	(6)	55	8	1	(1)	0.33	0.05	1	(1)	0.33	0.05	-		-	-	1	(1)	0.33	0.050	1	(1)	0.3	0.05
	-		-	-	-		-	-	2	(3)	0.67	0.10	-		-	-	3	(2)	1	0.15	1.5	(6)	0.5	0.8
	-		-	-	-		-	-	-		-	-	-		-	-	1	(3)	0.33	0.050	-		-	-
	-		-	-	-		-	-	-		-	-	-		-	-	0.3	(5)	0.10	0.015	-		-	-
ethion	0.06	(1)	0.02	0.003	720	(1)	240	36	210	(1)	70	11	173	(1)	58	9	500	(1)	167	25	7,600	(1)	2,533	380
	-		-	-	-		-	-	13	(3)	4.3	0.65	150	(4)	50	8	193	(3)	64	10	7,500	(4)	2,500	375
	-		-	-	-		-	-	22	(4)	7.3	1.1	-		-	-	560	(4)	187	28	-		-	-
heptachlor	-		-	-	23	(9)	8	1	13	(9)	4	1	10	(9)	3	1	8.0	(9)	2.7	0.4	25	(9)	8	1
hexazinone	151,600	(6)	50,533	7,580	274,000	(4)	91,333	13,700	100,000	(6)	33,333	5,000	-		-	-	180,000	(6)	60,000	9,000	-		-	-
metolachlor	23,500	(6)	7,833	1,175	-		-	-	15,000	(6)	5,000	750	-		-	-	2,000	(6)	667	100	4,900	(5)	1,633	245
metribuzin	4,200	(6)	1,400	210	-		-	-	80,000	(4)	26,667	4,000	-		-	-	64,000	(4)	21,333	3,200	1,000,000	(6)	33,333	5,000
norflurazon	15,000	(6)	5,000	750	-		-	-	16,300	(6)	5,433	815	-		-	-	8,100	(6)	2,700	405	>200,000	(4)	>67,000	>10,000
simazine	1,100	(6)	367	55	100,000	(6)	33,333	5,000	90,000	(4)	30,000	4,500	-		-	-	100,000	(6)	33,333	5,000	-		-	-

(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC_{50} is the lowest value which has been determined for a species significant to the indigenous aquatic community.

(#) Species is not indigenous. Information is given for comparison purposes only.

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(9) Mayer, F.L., and M.R. Ellersieck. (1986). Manual of Acute Toxicity: Interpretation and Database for 410 Chemicals and 66 Species of Freshwater Animals. U.S. Fish and Wildlife Service, Publication No. 160

Table 6. Atrazine Desethyl/Atrazine Ratio (DAR) Data.

DATE	SITE	FLOW*	atrazine ug/L	moles/L	atrazine desethyl ug/L	moles/L	DAR
11/8/1999	S38B	N	0.53	2.5E-09	0.038	2.0E-10	0.1
11/9/1999	S176	N	0.044	2.0E-10	0.0099	5.3E-11	0.3
	S178	N	0.019	8.8E-11	0.010	5.3E-11	0.6
11/16/1999	S78	Y	0.061	2.8E-10	0.01	5.3E-11	0.2
	CR33.5T	Y	0.070	3.2E-10	0.013	6.9E-11	0.2
	S79	Y	0.065	3.0E-10	0.013	6.9E-11	0.2
11/17/1999	S235	R	0.072	3.3E-10	0.015	8.0E-11	0.2
	S3	N	0.12	5.6E-10	0.014	7.5E-11	0.1
	S2	N	0.11	5.1E-10	0.022	1.2E-10	0.2
	S80	Y	0.13	6.0E-10	0.027	1.4E-10	0.2

DAR	all sites	flow only sites	no flow sites
average	0.2	0.2	0.3
median	0.2	0.2	0.2
minimum	0.1	0.2	0.1
maximum	0.6	0.2	0.6

* N – no Y – yes R- reverse

Figure 2. Ethion Concentration in Surface Water at S99

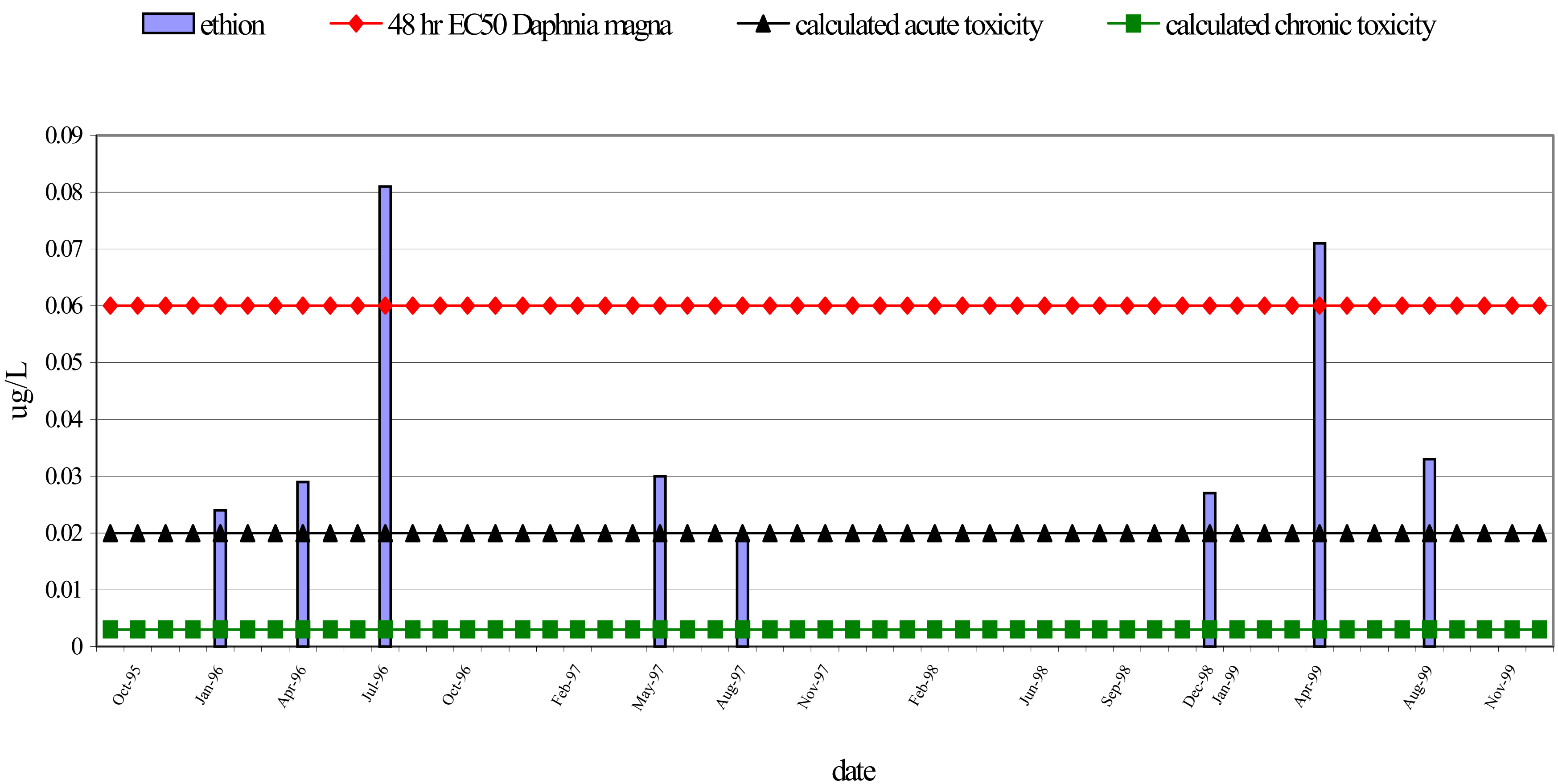

Figure 3. Endosulfan Concentration in Surface Water at S178